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Iron sequestration in young deep-sea sediments

Andre Baldermann (1), Laurence Warr (2), Ilse Letofsky-Papst (3), and Michael Böttcher (4)

(1) Institute of Applied Geosciences, Graz University of Technology, Graz, Austria (baldermann@tugraz.at), (2) Department of Geography and Geology, Greifswald University, Greifswald, Germany (warr@uni-greifswald.de), (3) Institute of Electron Microscopy and Nanoanalysis, Graz University of Technology, Graz, Austria (ilse.papst@felmi-zfe.at), (4) Marine Geology Department, Leibnitz-Institute for Baltic Sea Research, Warnemünde, Germany (michael.boettcher@io-warnemuende.de)

Iron is the fourth most abundant element in the Earth's crust and plays a key role in most surface processes. Despite being present in trace element concentrations in modern aqueous systems, iron is an essential nutrient for metabolic processes and valence state transformations provide a crucial energy source for microbial activity and growth as well as related biomineralization processes. Due to its close coupling with other element cycles such as the C, N, P and S, early diagenetic iron mineral phase transformations play an important role in determining the biogeochemical, mineralogical and petrological characteristics of modern marine sediments. Iron monosulfide and pyrite precipitation are currently considered to be the most important sink of iron and sulfur in mostly suboxic and aerobic marine systems, but the dynamics in the sediment's iron budget are notably complex.

The characteristics of superficial sediments from ODP Site 959, Ivory Coast-Ghana Marginal Ridge (Western African Coast) suggests that the majority of the highly reactive and potentially bioavailable iron input, which is mainly related to (nano)particulate amorphous Fe-oxyhydrates such as ferrihydrite, was directly utilized for green clay mineral authigenesis to form glauconite-smectite and glauconite minerals. Baldermann et al. (2013) investigated the Fe-smectite to glauconite reaction and suggested that iron could be the most important limiting factor for deep-water glauconitization at this site. Here we present combined electron energy loss spectroscopy data, high-resolution transmission electron microscopy images and chemical composition data of the authigenic green clay mineral particles at various burial depths beneath the water-sediment interface. The results clearly reveal strong Fe uptake with the increasing state of glauconitization from 3.0 - 6.0 wt.% of FeO to 24.8 - 26.2 wt.% of FeO+Fe2O_3, which represents a removal of between 7 to 54 mass.% of the total available iron (19 mass.% on average) within the upper 25 m of sediment. Within the first 3 meters of the sedimentary pile, iron sequestration related to green clay formation is $\sim$11 times higher than that of pyritization. Even at greater depths $\geq$ 3 mbsf, where the pyritization reaction becomes progressively more important and 29 to 66% of the initial detrital ferrihydrite input is almost dissolved, $\sim$50% of iron sequestration can be attributed to glauconitization. Initial mass balance calculations of the sediment's iron budget indicate that iron sequestration at ODP Site 959 is mainly controlled by the competing rates of pyritization and glauconitization. Iron sequestration associated with early diagenetic green clay formation could significantly impact the bioavailability of reactive iron in marine aqueous systems and thus influence both the marine iron cycle and deep biosphere environment. The role of deep-water glauconitization on iron availability and sequestration should be considered in future ocean-atmospheric models of the iron biogeochemical cycle.

Baldermann, A., Warr, L.N., Grathoff, G.H. & Dietzel, M. (2013) The rate and mechanism of deep-sea glauconite formation at the Ivory Coast-Ghana Marginal Ridge. Clays and Clay Minerals, 61, 258-276.